Thermodynamic Characteristics and Mechanism of Copper Monolayer Electrocrystallization from Sulphate Solution

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The thermodynamic characteristics of discharge and crystallization stages of metals electrodeposition are an essential argument in substantation of electrode process mechanism [1]. This approach which suggests partitioning of the overpotential to the summands of the discharge η_d and crystallization η_c overpotentials [2] has been utillized at the analysis of the galvanostatic copper monolayer growth on the copper polycrystallic electrode. The experiments have been carried out in the solution containing 1 M $CuSO_4$, 0.5 M H_2SO_4 on the copper coating butt platinum electrode. The exchange currents of discharge stage i_0 and crystallization stage v_0 and the "equilibrium" adatoms concentration c_0 have been determined from the potential transient curves by the method [3]. According to [4] from the temperature dependences of these parameters (4 – 40 °C) the heat effect $\Delta \vec{H}_c = -204 \pm 22 \, kJ \cdot mole^{-1}$, the entropy $\Delta \vec{S}_c = -510 \pm 70 \, J \cdot mole^{-1} \cdot K^{-1}$ and the activation enthalpie $\Delta \vec{H}_c^{\neq} = 212 \pm 54 \, kJ \cdot mole^{-1}$ of crystallyzation stage and the activation enthalpie of discharge stage $\Delta \vec{H}_d^{\neq} = 65 \pm 3 \, kJ \cdot mole^{-1}$ have been determined for equilibrium. The activation enthalpie of crystallization stage during growth $\Delta \vec{H}_{c(i)}^{\neq} = 64 \pm 8 \, kJ \cdot mole^{-1}$ hase been calculated from the $\eta_t, i -$ curves series obtaned after partitioning of the η_d and η_c overpotentials for the monolayer filling time. The indexes of the direct and backward directions are indicated according to the equation: $Cu_{ad} + p \Leftrightarrow Cu_p$, where p, Cu_{ad} and Cu_p note growth sites, copper adatoms on flat electrode spaces and in growth sites.

The comparison of the values of $\Delta \vec{H}_c$ and $\Delta \vec{H}_c^{\neq}$ shows that the $\Delta \vec{H}_c^{\neq}$ is in limits of the activation energy value of adatoms surface diffusion [1]. However according to the principle of microreversibility and in connection with the).

symmetry of surface diffusion energy barrier the relation $\Delta \vec{H}_c^{\neq} \cong \Delta \vec{H}_c$ should be fulfilled but it contradicts the experiment. The essential change of entropy does not answer checking role of surface diffusion also. In this connection the deduction about a slow adatoms incorporation into growth sites, which define crystallization overpotential, has been made. The values of $\Delta \vec{H}_c^{\neq}$ and $\Delta \vec{S}_c$ are in accordance with such mechanism: $\Delta \vec{H}_c^{\neq}$ is close to the theoretically rated quantity of activation enthalpy of copper adatoms exit from growth steps [1], and $\Delta \vec{S}_c$ corresponds to diminution of the freedom degrees number of adatoms in growth sites. The obtained results do not eliminate participation of adatoms (adions) surface diffusion in electrocrystallization but the values of the relative depth of penetration ($\lambda_0 / x_0 \cong 2.5$) prove a minor inhibition of this stage of process.

The given data corresponds the following mechanism of process. The Cu^{2+} ions reduction develops by steps; the $\Delta \vec{H}_d^{\neq}$ value answers a slow addition of the first electron and is close to the quantity calculated on the basis of the solvent reorganization theory [5]. Depending on the adatom (adions) diffusion flow density the further ions reduction happens or on flat surface spaces, or near to growth steps (direct discharge). According to [1] and the λ_0 / x_0 values the first case is more probable because it is stipulated by a partial charge transfer, and adions are the diffusing particles. The energy barrier $\Delta \vec{H}_{c(i)}^{\neq}$ (at equilibrium $\Delta \vec{H}_c^{\neq}$) controlling crystallization stage is determined by adions incorporation to growth steps or half-crystal positions.

References
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